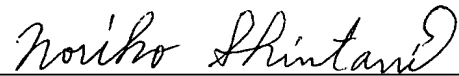


DECLARATION

I, Noriko SHINTANI, Patent Attorney, of SIKs & Co., 8th Floor, Kyobashi-Nisshoku Bldg., 8-7, Kyobashi 1-chome, Chuo-ku, Tokyo 104-0031 JAPAN hereby declare that I am the translator of the certified official copy of the documents in respect of an application for a patent filed in Japan on September 13, 2001 under Patent Application No. 277521/2001 and that the following is a true and correct translation to the best of my knowledge and belief.

Dated: September 27, 2005

A handwritten signature in cursive script, reading "Noriko Shintani", written in dark ink.

Noriko SHINTANI

PATENT OFFICE



This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application : September 13, 2001

Application Number : Patent Application No. 2001-277521
[ST.10/C]: [JP 2001-277521]

Applicant(s) : Mitsubishi Chemical Corporation

February 13, 2004

Yasuo IMAI

Commissioner, Patent Office

Certification No. 2004-3009240

[Title]	Application for Patent
[Reference Number]	A11289J
[Filing Date]	September 13, 2001
[Address]	To the Commissioner of the Patent Office
[Title of the Invention]	Cosmetic Polymer Composition and Cosmetic Using the Same
[Number of Claims]	17
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[List of Attached Documents]

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Specification 1

[Document's Name]

Abstract 1

[Number of Comprehensive Power of Attorney]

9805687

[Proof]

Required



English translation of Japanese Patent Application No. 2001-277521 (filed Sep. 13, 2001)

[Name of document] Specification

[Title of the invention] COSMETIC POLYMER COMPOSITION AND COSMETIC USING THE SAME

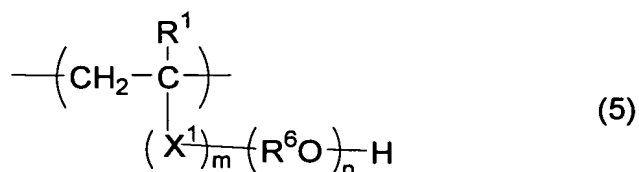
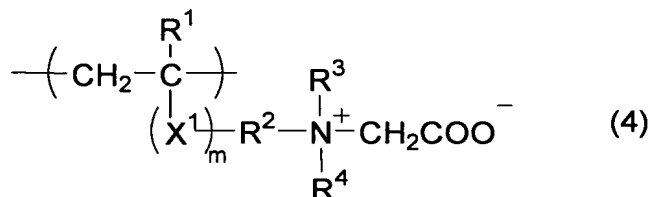
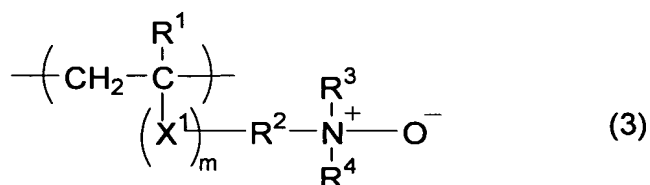
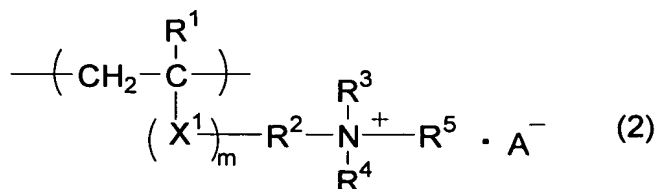
[Claims]

[Claim 1] A cosmetic polymer composition comprising a block copolymer having a unit derived from a compound having an ethylenic unsaturated bond, having a number-average molecular weight of 1.0×10^3 to 1.0×10^6 , and having two or more glass transition points or melting points.

[Claim 2] The cosmetic polymer composition as set forth in claim 1, wherein the block copolymer comprises at least one block composed of a unit having a hydrophilic group.

[Claim 3] The cosmetic polymer composition as set forth in claim 1 or 2, wherein the hydrophilic group is at least any one selected from groups consisting of an anionic group consisting of carboxylic acid group, sulfonic acid group, phosphonic acid group and salts of these groups; a cationic group consisting of amino group (including quaternary ammonium salt group), pyridyl group and salts of these groups; a nonionic group consisting of hydroxyl group, alkoxy group, epoxy group, amido group and cyano group; an amphoteric ionic group consisting of carboxybetaine group; and a semipolar group consisting of amine oxide group.

[Claim 4] The cosmetic polymer composition as set forth in any one of claims 1 to 3, wherein the block copolymer comprises at least one of units represented by formulae (1) to (5) below:



(where, R¹ represents a hydrogen atom or a methyl group; R² and R⁶ respectively represent a C₁₋₄ straight-chain or branched-chain alkylene group; R³, R⁴ and R⁵ respectively represent a hydrogen atom, C₁₋₂₄ alkyl group, C₆₋₂₄ aryl group, or any combination thereof such as C₇₋₂₄ arylalkyl group or alkylaryl group; and X¹ represents -COO-, -CONH-, -O- or NH-. A⁻ represents an anion; and M represents a hydrogen atom, an alkali metal ion or an ammonium ion. m is 0 or 1; and n is any integer from 1 to 50.)

[Claim 5] The cosmetic polymer composition as set forth in

any one of claims 1 to 4, wherein the block copolymer is a di-block copolymer, tri-block copolymer or multi-block copolymer.

[Claim 6] The cosmetic polymer composition as set forth in any one of claims 1 to 5, wherein the block copolymer comprises a unit derived from an ethylenic unsaturated carboxylic acid, and a unit derived from an ethylenic unsaturated carboxylate ester.

[Claim 7] The cosmetic polymer composition as set forth in any one of claims 1 to 6, wherein the block copolymer comprises the unit derived from an ethylenic unsaturated carboxylic acid in an amount of 10 to 90% by weight, and the unit derived from an ethylenic unsaturated carboxylate ester in an amount of 90 to 10% by weight.

[Claim 8] The cosmetic polymer composition as set forth in any one of claims 1 to 7, wherein the block copolymer comprises at least one block formed by post-treatment after polymerization.

[Claim 9] The cosmetic polymer composition as set forth in claims 8, wherein the post-treatment is hydrolysis.

[Claim 10] The cosmetic polymer composition as set forth in any one of claims 1 to 9, wherein the block copolymer has a glass transition point or a melting point nearly equal to a glass transition point or a melting point of a homopolymer composed of the monomer which make up at least one block of the block copolymer.

[Claim 11] The cosmetic polymer composition as set forth in any one of claims 1 to 10, wherein a block unit composing the block copolymer has a number-average molecular weight of

10³ to 10⁵.

[Claim 12] The cosmetic polymer composition as set forth in any one of claims 1 to 11, wherein weight-average molecular weight (Mw) and number-average molecular weight (Mn) of the block copolymer give a ratio (Mw/Mn) of 2.5 or less.

[Claim 13] The cosmetic polymer composition as set forth in any one of claims 1 to 12, wherein the block copolymer is dispersible or soluble in water and/or alcohol.

[Claim 14] The cosmetic polymer composition as set forth in any one of claims 1 to 13, wherein the block copolymer is produced by controlled radical polymerization using an organic halide as an initiator, and using, as a catalyst, at least a metal complex having a metal selected from Group VIII, Group IX, Group X and Group XI elements in the periodic table as a central metal.

[Claim 15] The cosmetic polymer composition as set forth in any one of claims 1 to 14, wherein the block copolymer is produced by controlled radical polymerization using a metal complex, derived from a copper halide and an amine compound, as a catalyst.

[Claim 16] A cosmetic employing a cosmetic polymer composition as set forth in any one of claims 1 to 15.

[Claim 17] The cosmetic as set forth in claim 16, used on hair, skin or nail.

[Detailed description of the invention]

[0001]

[Technical field of the invention]

The present invention relates to cosmetic polymer compositions comprising a block copolymer, and cosmetics

using the same, and more specifically relates to cosmetic polymer compositions and cosmetics using the same, containing a block copolymer having two or more units, which are introduced into the molecular skeleton thereof as block-wise unit, having different properties each other.

[0002]

[Related art]

There are known cosmetic materials containing a film-forming polymer, intended for use on skin, nail and hair. For example, for the purpose of improving makeup-lasting property, protecting skin or nail, or coloring or decorating skin or nail, film-forming polymers have been used in those for skin and nail. For the purpose of improving affinities to hairs or adhesiveness between hairs, and thereby having hair-style-keeping property, film-forming polymers have been used in those for hair. Examples of the polymer conventionally used for hair cosmetics include nonionic-base, anionic-base, cationic base and amphoteric-base ones. Although, as nonionic-base polymer, poly(vinyl methyl ether) or polyvinylpyrrolidone has been used, properties of polyvinylpyrrolidone are highly influenced by humidity conditions, and properties of a film formed of such a polymer are therefore also influenced by humidity conditions. More specifically, on one hand, the film before being moistened is hard and thus causative of flaking, but on the other hand, the film is considerably softened under a hot and humid environment so as to cause blocking, and tends to make it difficult to comb or brush the hair due to adhesion of hairs. Properties of poly(vinyl methyl ether)

are further significantly influenced by humidity condition.
[0003]

Examples of the anionic-base polymer include a copolymer of vinylcarboxylic acid having a carboxylic acid group as an anionic group (e.g., acrylic acid, methacrylic acid) and styrene or alkyl acrylic ester. Unlike the nonionic-base polymer, properties of the anionic-base polymer are less influenced by susceptible to humidity, but has a poor affinity to hair because of its anionic property as same as hair. Although the anionic-base polymer film is hard and excellent in hair styling property, on the other hand, it is rather brittle and highly causative of flaking. Moreover, its anionic property limits addition of any cationic substances, so that solidification typically due to rinse material (cationic) during hair wash is also anticipated. The cationic-base polymer has larger affinity to hair as compared with that of two aforementioned polymers, but its properties are influenced by humidity conditions as well as properties of the nonionic-polymer. Its cationic property also raises anticipation of toxicity or skin irritation property, limitation of addition of any anionic-base substances, and solidification caused by shampoo (anionic) during hair wash.

[0004]

Recently, there has been a need for alcohol-free hair cosmetic because of its merit of easy removal by hair wash, readiness in preparation of hair cosmetic simply by dilution with water, and environmental friendliness. From this point of view, a polymer used for the hair cosmetic is preferably

of water soluble. There is, however, a general problem that improving in water solubility of polymer contributes to lowering setting power. To overcome these drawbacks in the hair cosmetic materials containing the anionic-base polymer, cationic-base polymer and nonionic-base polymer, there are proposed cosmetic materials using an amphoteric polymer and polarized polymer which are copolymers having carboxybetaine or amine oxide as a hydrophilic group (see Japanese Laid-Open Patent Publication Nos. syo 51-9732, syo 55-104209 and hei 10-72323). The amphoteric polymer and polarized polymer are, however, disadvantageous in having only an insufficient compatibility with various cosmetic base materials.

[0005]

The aforementioned general-purpose ionic polymers have played a role of keeping hair styling through affinity to hair, film-formation property and adhesion property between hair yarns, while exhibiting the individual features. The styling materials using these general-purpose ionic polymers, however, suffer from a problem of tacky feeling under a moistened condition, and stiff feeling under a dried condition. For actual prescription, in order to improve such feelings, a small amount of oil is added to the polymer. Addition of the oil material, however, lowers ability of the polymer and makes it difficult to keep its intrinsically excellent setting ability. This raises a strong demand for developing a new polymer capable of keeping a plurality of good abilities such as setting ability or ability to give nice feeling, and can readily be removed by hair wash. Based on this situation, one

investigation have been made on a thermoplastic elastomer having a random-copolymerized principal chain and water soluble graft chains, and being soluble or dispersible in water or alcohol. This is, however, still on the way to achieve polymer elasticity sufficient for used as a cosmetic polymer composition (Published Japanese Translations of PCT International Publication for Patent Publications No. hei 8-512083, Japanese Laid-Open Patent Publication No. hei 11-181029).

[0006]

Some thermoplastic elastomeric copolymers are known, and typical examples thereof widely used include styrene butadiene copolymer, styrene-isoprene copolymer and hydrogen-added product of these copolymers (respectively referred to as styrene-ethylene-butylene copolymer and styrene-ethylene-propylene copolymer). These block copolymers have both of thermoplastic-like property, which contributes to solubility and strength of the copolymer, and rubber-like elasticity which contributes to flexibility and shape-retaining property. These block copolymers are also known to be available as a compatibilizing agent for various general-purpose thermoplastics. Most of the thermoplastic elastomeric copolymer are, however, generally insoluble or less soluble in aqueous and/or alcoholic solvent, and are not suitable for the cosmetic polymer composition. It should be useful in developing an improved cosmetic polymer composition if any thermoplastic elastomeric copolymer having the above-described properties and solubility in water and/or alcohol can be provided. It is also expected

that use of the above-described, water-soluble thermoplastic elastomer as a compatibilizing agent for general-purpose resins breaks a way to a polymer blend (combined use of an anionic polymer and a cationic polymer), which has been unpractical.

[0007]

[Problems to be solved by the invention]

As described above, general polymers conventionally used for setting hairs cannot give by themselves at the same time a plurality of abilities, such as high setting ability and good feeling in use, required for the cosmetic material, and, thus, such polymers have been used in combination with any polymer or any oil component to keep a certain level property. However, such additions of oil components or the like may bring about decreases of abilities originally given by the general polymers.

[0008]

The present invention is provided in order to solve the above mentioned problems, and one object of the present invention is to provide a cosmetic polymer composition and a cosmetic material capable of satisfying at the same time a plurality of abilities required for the cosmetic material by using a polymer having two or more properties. Another object of the present invention is to provide a cosmetic material having an excellent film-forming ability on hair, skin or nail, flexibility ascribable to its elasticity, and excellent feeling in use without contributing to tacky feeling nor uncomfortable feeling due to the film formation,

and is to provide also a cosmetic polymer composition capable of producing such cosmetic material.

[0009]

[Means of solving the problems]

Under the above circumstances, in order to solve the above mentioned problems, the present inventors conducted various studies, and as a result, they found that a block polymer exhibiting a specific physical property can give two contradictory performances such as good film flexibility and good film shape-keeping ability. They also found that such a polymer can still exhibit properties such as hydrophilicity required for preparing cosmetics or required environmentally. On the basis of these findings, the present invention was achieved. And, thus, one feature of a cosmetic polymer composition of the present invention resides in that the cosmetic polymer composition comprises a block copolymer having a unit derived from a compound having an ethylenic unsaturated bond, having a number-average molecular weight of 1.0×10^3 to 1.0×10^6 , and having two or more glass transition points or melting points. The block copolymer may be a di-block, tri-block or multi-block copolymer.

[0010]

As a preferred embodiment of the present invention, the cosmetic polymer composition wherein the block copolymer comprises at least one block composed of a unit having a hydrophilic group is provided. The hydrophilic group may be an anionic group, a cationic group, a nonionic group, an amphoteric ionic group or a semipolar group. As a more

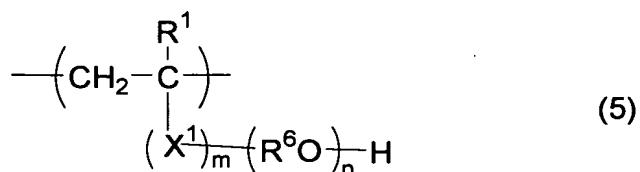
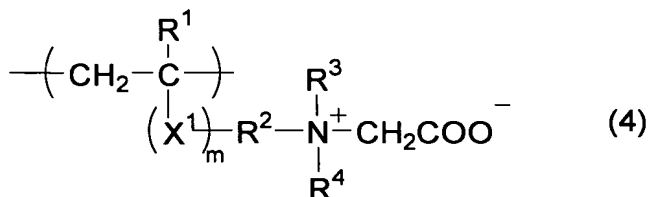
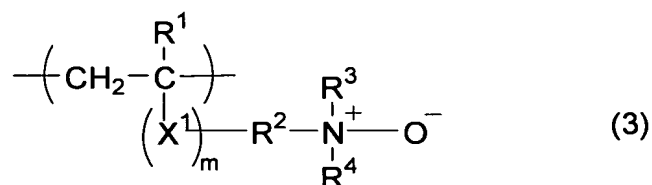
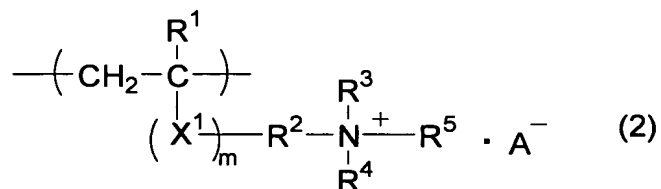
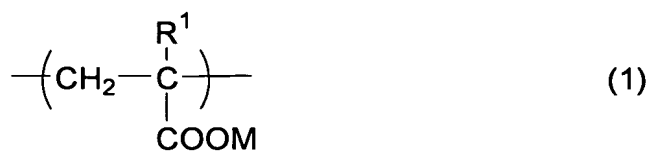
preferred embodiment of the present invention, the cosmetic polymer composition wherein the hydrophilic group is at least any one selected from groups consisting of an anionic group consisting of carboxylic acid group, sulfonic acid group, phosphonic acid group and salts of these groups; a cationic group consisting of amino group (including quaternary ammonium salt group), pyridyl group and salts of these groups; a nonionic group consisting of hydroxyl group, alkoxy group, epoxy group, amido group and cyano group; an amphoteric ionic group consisting of carboxybetaine group; and a semipolar group consisting of amine oxide group; is provided.

[0011]

As a preferred embodiment of the present invention, the cosmetic polymer composition wherein the block copolymer comprises at least one of units represented by formulae (1) to (5) below is provided.

[0012]

[Chemical Formula 2]



[0013]

In the formulae, R^1 represents a hydrogen atom or a methyl group; R^2 and R^6 respectively represent a C_{1-4} straight-chain or branched alkylene group; R^3 , R^4 and R^5 respectively represent a hydrogen atom, a C_{1-24} alkyl group, a C_{6-24} aryl group, or any combination thereof such as C_{7-24} arylalkyl group or alkylaryl group; and X^1 represents ---COO--- , ---CONH--- , ---O--- or NH--- . A^- represents an anion; and M represents a hydrogen atom, an alkali metal ion or an ammonium ion. m is 0 or 1; and n is any integer from 1 to

50.

[0014]

As preferred embodiments of the present invention, the cosmetic polymer composition wherein the block copolymer comprises a unit derived from an ethylenic unsaturated carboxylic acid, and a unit derived from an ethylenic unsaturated carboxylate ester; the cosmetic polymer composition wherein the block copolymer comprises the unit derived from an ethylenic unsaturated carboxylic acid in an amount of 10 to 90% by weight, and the unit derived from an ethylenic unsaturated carboxylate ester in an amount of 90 to 10% by weight; and the cosmetic polymer composition, wherein the block copolymer has a glass transition point or a melting point nearly equal to a glass transition point or a melting point of a homopolymer composed of the monomer which make up at least one block of the block copolymer; are provided.

It is noted that the term of "nearly equal to" is used not only for a situation of completely equal to each other and for a situation of permissibly equal to each other, but also for a situation of differing within 10 °C from each other.

[0015]

As preferred embodiments of the present invention, the cosmetic polymer composition, wherein the block copolymer comprises at least one block formed by post-treatment after polymerization; the cosmetic polymer composition, wherein a block unit composing the block copolymer has a number-average molecular weight of 10^3 to 10^5 ; and the cosmetic

polymer composition, wherein weight-average molecular weight (Mw) and number-average molecular weight (Mn) of the block copolymer give a ratio (Mw/Mn) of 2.5 or less; are provided.

It is noted that examples of the post-treatment include quaternization of nitrogen atoms, amine-oxide-forming treatment and hydrolysis of esters.

[0016]

As preferred embodiments of the present invention, the cosmetic polymer composition, wherein the block copolymer is dispersible or soluble in water and/or alcohol; the cosmetic polymer composition, wherein the copolymer is capable of forming a film having a Young's modulus of 50 MPa or more (more preferably 100 MPa or more), and an elongation percentage of 150% or more (more preferably 100 % or more); and the cosmetic polymer composition, wherein the block copolymer has a glass transition point or a melting point nearly equal to a glass transition point or a melting point of a homopolymer composed of the monomer which make up at least one block of the block copolymer; are provided.

[0017]

As preferred embodiments of the present invention, the cosmetic polymer composition, wherein the block copolymer is produced by controlled radical polymerization; the cosmetic polymer composition, wherein the block copolymer is produced by controlled radical polymerization using an organic halide as an initiator, and using, as a catalyst, at least a metal complex having a metal selected from Group VIII, Group IX, Group X and Group XI elements in the periodic table as a central metal; the cosmetic polymer composition, wherein the

block copolymer is produced by controlled radical polymerization using a metal complex, derived from a copper halide and an amine compound, as a catalyst; and the cosmetic polymer composition, wherein the block copolymer is produced according to a process comprising a polymerization step of carrying out a polymerization of a second compound having an ethylenic unsaturated bond using a homopolymer of a first compound having an ethylenic unsaturated bond to produce a copolymer comprising a first block derived from the first compound and a second block derived from the second compound and a post-treatment step of carrying out a post treatment of the first block and/or the second block to form a third block; are provided.

[0018]

In another aspect, the present invention provides a cosmetic employing the cosmetic polymer composition; and the cosmetic used on hair, skin or nail.

[0019]

[Embodiments for carrying out the invention]

Next paragraphs will further detail the present invention. It is to be noted that, in the present specification, a word "to" indicates a range including the numerical values placed therebefore and thereafter as a minimum value and a maximum value.

[0020]

The cosmetic polymer composition of the present invention comprises a block copolymer. The block copolymer has a unit derived from a compound having an ethylenic unsaturated bond, and has a number-average molecular weight

of 1.0×10^3 to 1.0×10^6 . The number-average molecular weight of the block copolymer exceeding 1.0×10^6 may result in an increased viscosity of the solution, and may raise a problem in its use as a cosmetic material. On the other hand, the number-average molecular weight less than 1.0×10^3 will result in a degraded film-forming ability, and may fail in achieving a sufficient performance in its use as a cosmetic material. A desirable range of the weight-average molecular weight of the block copolymer varies depending on purposes of use, and preferably falls in a range from 5.0×10^3 to 3.0×10^5 for use as a hair cosmetic material, in particular as a hair styling agent, and in a range from 2.0×10^4 to 1.5×10^5 for use as an agent for supplying a conditioning function. For use as cosmetic materials to be applied on skin and nail, the preferable range falls in a range from 1.0×10^4 to 5×10^5 , and more preferably from 2.0×10^4 to 1.0×10^6 .

[0021]

Although there is no specific limitation on the ratio (M_w/M_n) of weight-average molecular weight (M_w) to number-average molecular weight (M_n) of the block copolymer, measured by gel permeation chromatography, the ratio is preferably 2.5 or less, more preferably 2.0 or less, and still more preferably 1.8 or less. M_w/M_n exceeding 2.5 tends to degrade the uniformity of the block copolymer. The controlled radical polymerization process, described later, is successful in obtaining a uniform block copolymer having a small value of M_w/M_n .

[0022]

Although there is no specific limitation on the number-average molecular weight of the individual block components of the block copolymer, it preferably falls in a range from 1.0×10^3 to 1.0×10^5 , and more preferably from 5.0×10^3 to 1.0×10^5 . The number-average molecular weight small than 1.0×10^3 may tend to excessively lower the viscosity, and on the other hand, the number-average molecular weight exceeding 1.0×10^5 may tend to excessively increase the viscosity, so that it is preferably set within a aforementioned range depending on required performances of the polymer.

[0023]

The block copolymer of the present invention has two or more glass transition points or melting points. Of two glass transition points, the higher one is preferably 25°C or higher, more preferably 40°C or higher, and still more preferably 50°C or higher. Of two glass transition points, the lower one is preferably lower than 25°C , more preferably 0°C or lower, and still more preferably -20°C or lower. All of the melting points are preferably 25°C or around, or higher. The block copolymer preferably has a glass transition point or a melting point attributed to each block, and in other words, preferably has a glass transition point or a melting point nearly equal to the glass transition point or the melting point of a homopolymer composed of a monomer which makes up one block of the block copolymer. For example, a block copolymer of A-B type preferably has two glass transition points or melting points, where each of the glass transition points or melting

points is nearly equal to a glass transition point or a melting point individually attributed to homopolymers of A and B. On the other hand, a block copolymer of A-B-C type preferably has three glass transition points or melting points, where each of the glass transition points or melting points is nearly equal to a glass transition point or a melting point individually attributed to homopolymers of A, B and C.

[0024]

Glass transition point (T_g) and melting point (T_m) refer to temperatures at which the polymer or a part thereof transits from a state of brittle material or solid into a state of rubber-like material or liquid, and can typically be measure by the differential scanning calorimetry. Glass transition phenomenon of polymer is described in "Introduction to Polymer Science and Technology", An SPE Textbook (eds. H. S. Kaufman and J.J. Falcetta), published by John Wiley & Sons (1977).

[0025]

The block copolymer comprising at least one block having a hydrophilic group can readily be removed by hair wash, and is therefore preferably used for hair cosmetic material having an excellent hair washing property. The block having a hydrophilic group is also advantageous in allowing the block copolymer to be blended with cosmetic materials in various forms. The hydrophilic group may be any of anionic group, cationic group, nonionic group and amphoteric group. Examples of the anionic group include carboxylic acid group, sulfonic acid group, phosphonic acid

group and salts of these groups; examples of the cationic group include amino group (including quaternary ammonium group), pyridyl group and salts of these groups; examples of the nonionic group include hydroxyl group, alkoxy group, epoxy group, amido group and cyano group; examples of the amphoteric ionic group include carboxybetaine group, sulfobetaine group and phosphobetaine group; and examples of the semipolar group include amine oxide group. These hydrophilic groups can be introduced into the block copolymer by polymerizing a monomer originally having the hydrophilic group, or by subjecting the copolymer after being polymerized to a post-treatment such as hydrolysis.

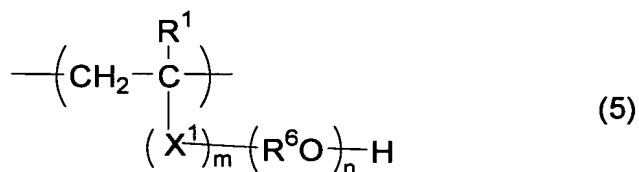
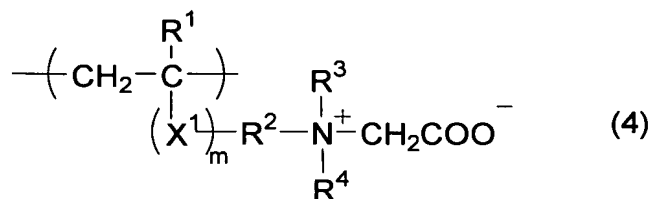
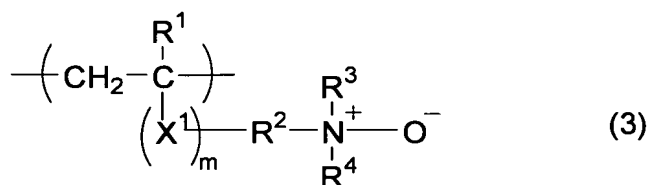
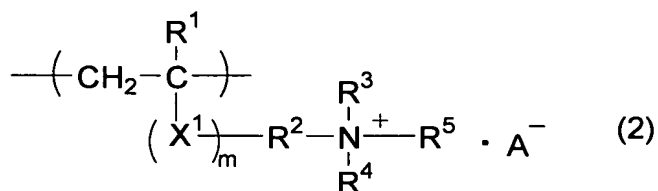
It is to be noted that the semipolar group in the context of this patent specification does not mean an apparent ionic group, but instead means a group having both features of ionic bond and covalent bond, and having a biased electron distribution.

[0026]

The block copolymer has a unit derived from a compound having an ethylenic unsaturated bond. As described in the above, at least one block of the block copolymer preferably has a hydrophilic group. The unit having a hydrophilic group is preferably any one of units represented by the formulae (1) to (5) below.

[0027]

[Chemical structure 3]



[0028]

In the formulae, R^1 represents a hydrogen atom or a methyl group; R^2 and R^6 respectively represent a C_{1-4} straight-chain or branched alkylene group; R^3 , R^4 and R^5 respectively represent a hydrogen atom, a C_{1-24} alkyl group, a C_{6-24} aryl group, or any combination thereof such as C_{7-24} arylalkyl group or alkylaryl group; and X^1 represents ---COO--- , ---CONH--- , ---O--- or NH--- . A^- represents an anion; and M represents a hydrogen atom, an alkali metal ion or an ammonium ion. m is 0 or 1; and n is any integer from 1 to

50.

[0029]

The C₁₋₂₄ alkyl group respectively represented by R³, R⁴ and R⁵ include all of straight-chain, branched-chain and cyclic alkyl groups. The same will apply also to the alkyl group portion of the arylalkyl group and the alkyl group portion of alkylaryl group represented respectively by R³, R⁴ and R⁵.

[0030]

Anion represented by A⁻ is exemplified by anionic group of acid, and specific examples thereof include halogen ion, sulfate ion and COO⁻. Alkali metal ion represented by M can be exemplified by Na⁺ and K⁺. Examples of ammonium ion represented by M not only include NH₄⁺ derived from ammonia, but also include alkylammonium ions derived from amines such as volatile amines such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, *n*-propylamine, *n*-butylamine, allylamine, ethylenediamine, morpholine and pyridine; and non-volatile amines such as mono-, di- or triethanolamine, mono-, di- or triisopropanolamine, aminoethyl propanol, aminoethyl propanediol and lysine.

[0031]

The block containing unit represented by any of the foregoing formulae (1) to (5) can be manufactured by using, as a monomer, a double-bond-containing compound corresponded to any of the units represented by the formulae (1) to (5). Even for the case where the compounds corresponded to the units represented by the formulae (1) to (5) are not used,

the block can be manufactured by polymerizing other monomer and subjecting the product to post-treatment such as hydrolysis. For example, a block copolymer having a block composed of the unit represented by the formula (1) can be manufactured also by using (meth)acrylic ester as a copolymerization monomer, in which a copolymer having a block composed of such monomer is synthesized, and the obtained block is then hydrolyzed. The block copolymer may be such as having two or more species of the blocks composed of the unit represented by any of the formulae (1) to (5).

[0032]

Examples of the compounds having ethylenic unsaturated bond, capable of composing the block copolymer, (including examples of the compounds capable of forming the units represented by the formulae (1) to (5)) are listed below, where the present invention is by no means limited by these specific examples.

Specific examples of the nonionic monomers include acrylic esters such as unsaturated methyl acrylate, ethyl acrylate, *n*-propyl acrylate, isopropyl acrylate, *n*-butyl acrylate, isobutyl acrylate, *t*-butyl acrylate, *n*-pentyl acrylate, *n*-hexyl acrylate, cyclohexyl acrylate, *n*-heptyl acrylate, *n*-octyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, decyl acrylate, dodecyl acrylate, phenyl acrylate, tolyl acrylate, benzyl acrylate, isobornyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, stearyl acrylate, glycidyl acrylate, 2-aminoethyl acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, γ -

(methacryloyloxypropyl)dimethoxysilane, ethylene oxide adduct of acrylic acid, trifluoromethylmethyl acrylate, 2-trifluoromethylethyl acrylate, 2-perfluoroethylethyl acrylate, 2-perfluoroethyl-2-perfluorobutylethyl acrylate, 2-perfluoroethyl acrylate, perfluoromethyl acrylate, diperfluoromethyl methyl acrylate, 2-perfluoromethyl-2-perfluoroethyl methyl acrylate, 2-perfluorohexyl ethyl acrylate, 2-perfluorodecyl ethyl acrylate and 2-perfluorohexadecyl ethyl acrylate; aromatic alkenyl compounds such as styrene, α -methylstyrene, *p*-methylstyrene, and *p*-methoxystyrene; vinyl cyanide compounds such as acrylonitrile and methacrylonitrile;

[0033]

conjugated diene-base compounds such as butadiene and isoprene; halogen-containing unsaturated compounds such as vinyl chloride, vinylidene chloride, perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing unsaturated compounds such as vinyl trimethoxysilane and vinyl triethoxysilane; unsaturated dicarboxylic acid compounds such as maleic anhydride, maleic acid, monoalkyl ester and dialkylester of maleic acid, fumaric acid, and monoalkyl ester and dialkyl ester of fumaric acid; vinyl ester compounds such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; maleimide-base compounds such as maleimide, methyl maleimide, ethyl maleimide, propyl maleimide, butyl maleimide, hexyl maleimide, octyl maleimide, dodecyl maleimide, stearyl maleimide, phenyl maleimide and cyclohexyl maleimide; methacrylic esters such as methyl

methacrylate, ethyl methacrylate, *n*-propyl methacrylate, isopropyl methacrylate, *n*-butyl methacrylate, isobutyl methacrylate, *tert*-butyl methacrylate, *n*-pentyl methacrylate, *n*-hexyl methacrylate, cyclohexyl methacrylate, *n*-heptyl methacrylate, *n*-octyl methacrylate, 2-ethylhexyl methacrylate, nonyl methacrylate, decyl methacrylate, dodecyl methacrylate, phenyl methacrylate, tolyl methacrylate, benzyl methacrylate, isobornyl methacrylate, 2-methoxyethyl methacrylate, 3-methoxybutyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, stearyl methacrylate, glycidyl methacrylate, 2-aminoethyl methacrylate, γ -(methacryloyloxypropyl)trimethoxy silane, γ -(methacryloyloxypropyl)dimethoxy methyl silane, ethylene oxide adduct of methacrylic acid, trifluoromethyl methyl methacrylate, 2-trifluoromethyl ethyl methacrylate, 2-perfluoroethyl ethyl methacrylate, 2-perfluoroethyl-2-perfluorobutyl ethyl methacrylate, 2-perfluoroethyl methacrylate, perfluoromethyl methacrylate, diperfluoromethyl methyl methacrylate, 2-perfluoromethyl-2-perfluoroethyl methyl methacrylate, 2-perfluorohexyl ethyl methacrylate, 2-perfluorodecyl ethyl methacrylate, and 2-perfluorohexadecyl ethyl methacrylate;

[0034]

monomers derived from (meth)acrylate or (meth)acrylamide with C₂₋₄ alkylene oxide such as hydroxyethyl (meth)acrylate, polyethylene glycol (meth)acrylate, methoxypoly(ethylene glycol/propylene glycol)mono(meth)acrylate, polyethylene glycol di(meth)acrylate and N-polyalkyleneoxy(meth)acrylamide; and hydrophilic nonionic

monomers such as N-cyclohexyl maleimide, N-phenylmaleimide, N-vinylpyrrolidone, N-(meth)acryloyl morpholine and acrylamide.

[0035]

Specific examples of anionic monomer include unsaturated carboxylic acid compounds such as (meth)acrylic acid, maleic acid, maleic anhydride, itaconic acids, fumaric acid and crotonic acid; half ester compounds derived from an unsaturated polybasic acid anhydride (e.g., succinic anhydride, phthalic anhydride) and a hydroxyl-group-containing (meth)acrylate (e.g., hydroxyethyl (meth)acrylate); compounds having a sulfonic acid group such as styrenesulfonic acid and sulfoethyl (meth)acrylate; and compounds having a phosphonic acid group such as acid phosphoxyethyl(meth)acrylate. There anionic unsaturated monomer can be used in a form of intact acid or partially-neutralized or completely-neutralized form, or can be subjected to copolymerization in a form of intact acid and can partially or completely be neutralized. Examples of the base used for the neutralization include alkali metal hydroxide such as potassium hydroxide and sodium hydroxide; aqueous ammonia solution; and amine compounds such as mono-, di- and tri-ethanolamines, and trimethylamine.

[0036]

Specific examples of cationic monomer include cationic monomers obtained by cationizing N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylaminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-diethylaminopropyl(meth)acrylate, N,N-

dimethylaminoethyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, *p*-dimethylaminomethyl styrene, *p*-dimethylaminoethyl styrene, *p*-diethylaminomethyl styrene or *p*-diethylaminoethylstyrene using a cationizing agent (e.g., alkyl halides such as methyl chloride, methyl bromide and methyl iodide; dialkyl sulfates such as dimethyl sulfate; epichlorohydrin-adduct of tertiary amine mineral acid salt such as N-(3-chloro-2-hydroxypropyl)-N,N,N-trimethylammonium chloride; inorganic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid and phosphoric acid; and carboxylic acids such as formic acid, acetic acid and propionic acid).

[0037]

Specific examples of amphoteric monomer include compounds obtained by reacting the above-described examples of the cationic monomer precursors with a modifying agent such as sodium haloacetate or potassium. specific examples of polarized monomer include amine oxides of N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N,N-dimethylaminopropyl (meth)acrylate, N,N-diethylaminopropyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, vinyl N,N-dimethylaminopropionate, *p*-dimethylaminomethylstyrene, *p*-dimethylaminoethylstyrene, *p*-diethylaminomethylstyrene and *p*-diethylaminoethylstyrene. These monomers can be used in a singular manner or in any combination of two or more

species.

[0038]

Among these, acrylic esters, methacrylic esters, aromatic alkenyl compounds, vinyl cyanide compounds, conjugate diene-base compounds or halogen-containing unsaturated compounds are preferably used in view of its readiness in industrial availability.

[0039]

A preferable embodiment of the block copolymer can be exemplified by a block copolymer comprising at least one species each of a block composed of an ethylenic unsaturated carboxylic acid unit, and a block composed of an ethylenic unsaturated carboxylate ester unit. The ethylenic unsaturated carboxylic acid unit is preferably a unit which is derived from a hydrophilic monomer and has a high Tg. Preferred examples of such a unit include units derived from acrylic acid and methacrylic acid. On the other hand, the ethylenic unsaturated carboxylate ester unit is preferably a unit which is derived from a hydrophobic monomer and has a low Tg. Preferred examples of such a unit include units derived from acrylic esters and methacrylic esters. Compositional ratios of the ethylenic unsaturated carboxylic acid block and the ethylenic unsaturated carboxylate ester block composing the polymer are preferably 10 to 90% by weight for the former, and 90 to 10% by weight for the latter, more preferably 15 to 80% by weight for the former, and 80 to 15% by weight for the latter, and still more preferably 20 to 50% by weight for the former and 80 to 50% by weight for the latter when more flexibility is desired.

On the other hand, when some kind of rigidity is required, the ratio of the former is preferably 80 to 50 % and the ratio of the latter is preferably 20 to 50 %. The ethylenic unsaturated carboxylic acid block less than 10% by weight tends to make the block copolymer insoluble into water, and the ethylenic unsaturated carboxylate ester block less than 10% by weight tends to worsen the film-forming ability and to considerably degrade rubber elasticity of the polymer.

It is to be noted that "unit derived from a compound" in the context of this patent specification means not only a unit obtained after polymerizing the compound as a monomer, but also means a unit structurally derived from the compound obtained after the post-treatment such as hydrolysis as described in the above.

[0040]

The block copolymer may have any form of diblock copolymer, triblock copolymer and multi-block copolymer, without departing from the straight-chain structure. For example, the block copolymer having a hard block A (high-Tg block) and a soft block B (low-Tg block) may have any form of A-B diblock copolymer, A-B-A triblock copolymer, B-A-B triblock copolymer and (A-B)_n multi-block copolymer. Among theses, A-B-A triblock copolymer, (A-B)_n multi-block copolymer and mixture of these are preferable in view of providing rubber elasticity to the polymer.

[0041]

The block copolymer may have a straight-chain structure or a branched-chain (star-shaped) structure, and may be selected from any mixtures thereof. The block

copolymer having any structure may be used depending on the required properties.

[0042]

The block copolymer is preferably dispersible or soluble in water and/or alcohol. The solubility in water (or solubility in alcohol) of the block copolymer can be confirmed by stirring 1 weight part of the block copolymer and 99 parts by weight of deionized water and/or ethanol-mixed solution at 60°C for 2 hours, cooling the mixture, allowing the mixture to stand at room temperature for a day, and observing that the resultant aqueous solution is kept homogeneous without producing precipitate, and the resultant aqueous solution shows a light transmissivity of 70% or more at 655 nm. "Dispersible" in the context of this patent specification means that fine particles of the copolymer can disperse in water and/or alcohol without causing precipitation, and is kept in an emulsified form or latex form.

[0043]

The block copolymer is preferably capable of forming a film having a Young's modulus of 50 MPa or more, and an elongation percentage of 150% or more; and is more preferably capable of forming a film having a Young's modulus of 100 MPa or more, and an elongation percentage of 200% or more. Young's modulus and elongation percentage can be measured by a film tensile test conforming to JIS K7161. If the block copolymer can form a film having Young's modulus and elongation percentage within the above-described ranges, the cosmetic polymer composition of the present

invention applied to a hair cosmetic material is successful in ensuring a desirable styling ability, and in providing a hair cosmetic material excellent in the feel of touch.

[0044]

The block copolymer is preferably manufactured by controlled polymerization. The controlled polymerization can be exemplified by living anionic polymerization, radical polymerization using a chain-transfer agent, and recently-developed living radical polymerization. Among these, living radical polymerization, a sort of controlled radical polymerization, is preferable because the method is successful in readily controlling the molecular weight and structure of the resultant block copolymer.

[0045]

Living radical polymerization refers to a radical polymerization during which activity of the polymerization terminal is kept without being lost. Living polymerization in a narrow sense refers to polymerization during which the terminal keeps on maintaining the activity, but is generally understood as including also pseudo-living polymerization in which inactivated terminal and activated terminal are kept in an equilibrium. The latter meaning is adopted in this patent specification. In recent years, living radical polymerization has extensively been studied by many teams, and known achievements include a method using a chain-transfer agent such as polysulfide; methods using radical trapping agents such as cobalt porphyrin complex (J. Am. Chem. Soc., 1994, 116, 7943) and nitroxide compound (Macromolecules, 1994, 27, 7228); and atom-transfer radical

polymerization (ATRP) using an organic halide as an initiator, and using a transition metal complex as a catalyst. Any of these methods may be adopted to the present invention, where atom-transfer radical polymerization is preferably adopted in view of simplicity in the control.

[0046]

In atom-transfer radical polymerization, organic halide or halogenated sulfonyl compound can be used as an initiator, and a metal complex, having a metal selected from Group VIII, Group IX, Group X and Group XI elements in the periodic table as a central metal, can be used as a catalyst. Specific processes of the atom-transfer radical polymerization, typically described by Matyjaszewski *et al.* (J. Am. Chem. Soc. 1995, 117, 5614; Macromolecules, 1995, 28, 7901 and Science, 1996, 272, 866) and by Sawamoto *et al.* (Macromolecules, 1995, 28, 1721), are preferably used also for the present invention. These methods can successfully proceed in a living manner despite that the polymerization speed is extremely large and the radical polymerization system is highly causative of termination reaction typically due to inter-radical coupling, and can produce a polymer having a narrow molecular weight distribution, namely has a M_w/M_n of 1.1 to 1.5 or around. The molecular weight can freely be controlled by charged amount ratio of the monomer to initiator.

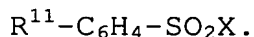
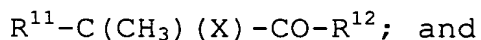
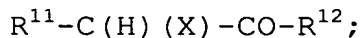
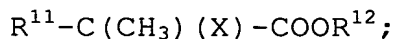
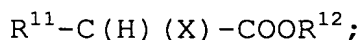
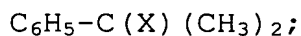
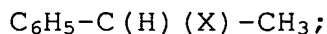
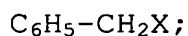
[0047]

In the atom-transfer radical polymerization, mono-functional, bi-functional or poly-functional organic halide,

or halogenated sulfonyl compound can be used as an initiator. These may appropriately be selected depending on purposes, where mono-functional compound is preferably used as an initiator for the manufacture of the diblock copolymer, bi-functional compound is preferably used for the manufacture of the triblock copolymer, and multi-functional compound is used for manufacture of the branched block copolymer.

[0048]

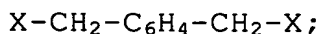
Examples of the mono-functional compounds which can be used as an initiator are listed below:



In these formulae, C_6H_4 represents a phenylene group (any of ortho-substitute, meta-substitute and para-substitute allowable). R^{11} represents a hydrogen atom, $\text{C}_1\text{-20}$ alkyl group, $\text{C}_6\text{-20}$ aryl group or $\text{C}_7\text{-20}$ aralkyl group. X represents chlorine, bromine or iodine. R^{12} represents a $\text{C}_1\text{-20}$ mono-valent organic group.

[0049]

Examples of the bi-functional compounds which can be used as an initiator are listed below:



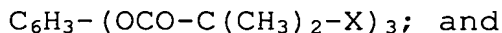
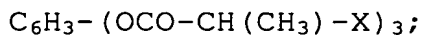
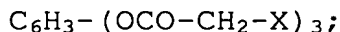
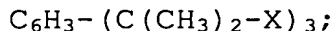
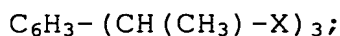
$X-CH(CH_3)-C_6H_4-CH(CH_3)-X;$
 $X-C(CH_3)_2-C_6H_4-C(CH_3)_2-X;$
 $X-CH(COOR^{13})-(CH_2)_n-CH(COOR^{13})-X;$
 $X-C(CH_3)(COOR^{13})-(CH_2)_n-C(CH_3)(COOR^{13})-X;$
 $X-CH(COR^{13})-(CH_2)_n-CH(COR^{13})-X;$
 $X-C(CH_3)(COR^{13})-(CH_2)_n-C(CH_3)(COR^{13})-X;$
 $X-CH_2-CO-CH_2-X;$
 $X-CH(CH_3)-CO-CH(CH_3)-X;$
 $X-C(CH_3)_2-CO-C(CH_3)_2-X;$
 $X-CH(C_6H_5)-CO-CH(C_6H_5)-X;$
 $X-CH_2-COO-(CH_2)_n-OCO-CH_2-X;$
 $X-CH(CH_3)-COO-(CH_2)_n-OCO-CH(CH_3)-X;$
 $X-C(CH_3)_2-COO-(CH_2)_n-OCO-C(CH_3)_2-X;$
 $X-CH_2-CO-CO-CH_2-X;$
 $X-CH(CH_3)-CO-CO-CH(CH_3)-X;$
 $X-C(CH_3)_2-CO-CO-C(CH_3)_2-X;$
 $X-CH_2-COO-C_6H_4-OCO-CH_2-X;$
 $X-CH(CH_3)-COO-C_6H_4-OCO-CH(CH_3)-X;$
 $X-C(CH_3)_2-COO-C_6H_4-OCO-C(CH_3)_2-X;$ and
 $X-SO_2-C_6H_4-SO_2-X.$

In these formulae, R^{13} represents a C_{1-20} alkyl group, C_{6-20} aryl group or C_{7-20} aralkyl group, where two or more R^{13} groups exist in one molecule may be same or different each other. C_6H_4 represents a phenylene group (any of ortho-substitute, meta-substitute and para-substitute allowable). C_6H_5 represents a phenyl group, n is an integer from 0 to 20, and X represents chlorine, bromine or iodine.

[0050]

Examples of the poly-functional compounds which can be

used as an initiator are listed below:



In these formulae, C_6H_3 represents a three-substituted phenyl group (any position of substituents on the 1- to 6-positions allowable). X represents chlorine, bromine or iodine.

[0051]

Use of organic halide or halogenated sulfonyl compound having a functional group not contributable to initiation of the polymerization is successful in readily obtaining a polymer having such functional group on the molecular terminal. Examples of the functional group can be exemplified by alkenyl group, hydroxyl group, epoxy group, amino group, amido group and silyl group.

[0052]

The organic halide and halogenated sulfonyl compound which can be used as an initiator are such as those having an activated carbon-halogen bond, the carbon of which is also bound to a carbonyl group, phenyl group or the like, thereby exhibiting the polymerization initiation property. The amount of use of the initiator may be determined in terms of ratio to the monomer, considering the molecular weight required for the block copolymer. In other words,

the molecular weight of the block copolymer can be controlled by the number of monomer molecules used per one initiator molecule.

[0053]

The transition metal catalyst used as a catalyst in the atom-transfer radical polymerization is not specifically limited, where preferable examples include monovalent and zero-valent copper, divalent ruthenium, divalent iron and divalent nickel complexes. Among these, copper complex is preferably used in view of cost and controllability of the reaction. When the complex is used as the metal catalyst, the complex may preliminarily be synthesized and added to the polymerization system, or may be produced in the system by adding a metal salt and ligand capable of forming a complex with the metal through coordinate bond respectively into the polymerization system. Among these, a preferable method is such as using copper halide as the metal catalyst together with an amine compound capable of forming coordinate bond with copper, and adding these substances into the polymerization system.

[0054]

Monovalent copper compounds which can be used as a catalyst for the atom-transfer radical polymerization can be exemplified typically by copper (I) chloride, copper (I) bromide, copper (I) iodide, copper (I) cyanide, copper (I) oxide and copper (I) perchlorate. The copper compound can preferably be used together with a ligand for enhancing the catalytic activity, and examples of the ligand include 2,2'-bipyridyl and its derivatives, 1,10-phenanthroline and its

derivatives, and polyamines such as tetramethylethylenetriamine (TMEDA), pentamethyldiethylenetriamine and hexamethyl(2-aminoethyl)amine. Divalent tris-triphenylphosphine complex of ruthenium ($\text{RuCl}_2(\text{PPh}_3)_3$) is also preferable as the catalyst. Use of ruthenium as the catalyst may preferably be associated with addition of aluminum alkoxide as an activator. Also bis-triphenylphosphine complex of divalent iron ($\text{FeCl}_2(\text{PPh}_3)_2$), bis-triphenylphosphine complex of divalent nickel ($\text{NiCl}_2(\text{PPh}_3)_2$), and bis-tributylphosphine complex of divalent nickel ($\text{NiBr}_2(\text{PBu}_3)_2$) are good catalysts. There are no specific limitations on the catalyst to be used, and amount of use of the ligand and activator, and may appropriately be determined considering relations with the amounts of initiator, monomer and solvent, and a desired reaction speed.

[0055]

The atom-transfer radical polymerization can be proceeded under a solventless condition (bulk polymerization) or in a variety of solvents. Examples of available solvents include hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, *n*-butanol and *t*-butanol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; carbonate

solvents such as ethylene carbonate and propylene carbonate; and other solvents such as dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone and water. These solvents may be used in a singular manner or as a mixture of two or more species. The solventless process is referred to as bulk polymerization as described in the above. On the other hand, when any solvent is used, the amount of addition of the solvent may appropriately be determined considering relation between viscosity of the entire system and necessary stirring efficiency (i.e., reaction speed).

[0056]

The atom-transfer radical polymerization can be proceeded within a range from room temperature to 200°C, and more preferably from 50 to 150°C.

[0057]

Specific methods for manufacturing the block copolymer based on the atom-transfer radical polymerization include a method in which the monomer is sequentially added; a method in which a preliminarily-synthesized polymer is used as a polymer initiator for polymerizing the next block; and a method in which separately-prepared monomers are allowed to bind through reaction. These methods may properly be selected depending on purposes, where the method based on the sequential addition of the monomer or use of the polymer initiator are preferable in view of simplicity of the manufacturing process.

[0058]

There is no specific limitation on the method of manufacturing the block copolymer, where the controlled

radical polymerization based on the sequential addition of the monomers using copper halide as a catalyst together with amine ligand is preferable since such method is successful in facilitating control of the molecular weight of the resultant block copolymer. In particular, use of dimethylformamide as a reaction solvent is more preferable because the reaction speed can be increased based on chelate effect with respect to the catalyst.

[0059]

The block copolymer obtained by the polymerization may be used for the cosmetic polymer composition of the present invention in an intact form, or used after being subjected to the post-treatment such as hydrolysis. Control of the modification ratio by the post-treatment is successful in adjusting various characteristics of the resultant block copolymer, such as water solubility and film-forming ability, within a desirable range adaptive to the applications. Examples of the post-treatment include hydrolysis, quaternization and amine-oxide-forming treatment. An exemplary hydrolytic process can hydrolyze a block formed of acrylic ester, methacrylic ester or the like, to thereby produce an acrylic acid-derived or methacrylic acid-derived block having carboxylic acid group as a hydrophilic group (e.g., a block having the unit represented by the formula (1)). Hydrolysis of ester can be carried out by using an acid catalyst such as hydrochloric acid and *p*-toluenesulfonic acid, or a base catalyst such as sodium hydroxide. The degree of hydrolysis can be controlled by the amount of use of the catalyst and reaction

time. The carboxylic acid thus produced by the hydrolysis may be used after being partially or completely neutralized. A substance conveniently used for the neutralization is base, and examples of the base include alkali metal hydroxide such as potassium hydroxide and sodium hydroxide; and amine compounds such as aqueous ammonia solution, mono-, di- and tri-ethanolamines and trimethylamine.

[0060]

Quaternization of a block composed of amino-group-containing methacrylate or the like can produce a block having a cationic quaternary ammonium group (e.g., the block represented by the formula (2)). The quaternization can be proceeded by using a cationizing agent, examples of which include alkyl halides such as methyl chloride, methyl bromide and methyl iodide; dialkyl sulfates such as dimethyl sulfate; epichlorohydrin-adduct of tertiary amine mineral acid salt such as N-(3-chloro-2-hydroxypropyl)-N,N,N-trimethylammonium chloride; inorganic acids such as hydrochloric acid, hydrobromic acid, sulfuric acid and phosphoric acid; and carboxylic acids such as formic acid, acetic acid and propionic acid). It is also possible to form a block having amine oxide group, which is a polarized group, by subjecting a block composed of amino-group-containing methacrylate or the like to amine-oxide-forming treatment (e.g., the block represented by the formula (3)). The amine-oxide-forming treatment can be carried out by using peracids such as hydrogen peroxide, ammonium persulfate, sodium persulfate, peracetic acid, meta-chloroperbenzoic acid, benzoyl peroxide, t-butylhydro

peroxide and so forth; and an oxidizing agent such as ozone.
[0061]

The cosmetic polymer composition of the present invention is applicable to cosmetic materials of various purposes. Among these, hair cosmetic material, skin cosmetic material and nail cosmetic material are preferable applications. The block copolymer can be provided as a polymer showing various characteristics required for various cosmetic materials, by determining composition of the individual blocks, for example, taking a hard/soft balance, and a hydrophilicity/hydrophobicity balance into consideration. For example, a cosmetic material containing the block copolymer composed of a hydrophilic segment, high-strength segment and high-elasticity segment can provide a hair cosmetic material having a desirable styling performance, no fear of becoming tacky under a moist condition nor becoming stiff under a dry condition, and a good hair washability which ensures easy-removing property with water. By similarly adjusting segment composition of the block copolymer and composition of each segment, the block copolymer can be provided also as a skin cosmetic material capable of uniformly spreading over the skin, being felt comfortable to the skin, and allowing medically active agent or the like to infuse through the skin. By similarly adjusting segment composition of the block copolymer and composition of each segment, the block copolymer can be provided also as a nail cosmetic material capable of uniformly spreading over the nail, readily forming a film, and ensuring an excellent film-retaining property.

[0062]

The individual cosmetic materials will be detailed in the next.

(Hair cosmetic Material)

The cosmetic polymer composition of the present invention is applicable to hair cosmetic materials of various purposes, such as shampoo, rinse, treatment, styling agent and permanent wave liquid and the like, and is also applicable in any form of liquid, cream, emulsion, gel, mousse or the like. For example, the block copolymer can be added to publicly-known hair cosmetic materials such as shampoo, rinse, treatment, styling agent and permanent wave liquid, in place of any publicly-known polymers. It is also allowable to use the block copolymer together with the publicly-known polymer of conventional use. Although a preferable range of content of the block copolymer in the hair cosmetic material may differ depending on forms and purposes of the hair cosmetic material, and also on types and amount of other materials to be used in combination, the block copolymer is preferably contained in an amount of 0.01 to 10% by weight of the hair cosmetic material.

[0063]

The next paragraphs will detail embodiments of the present invention applied to the hair cosmetic materials.

(1) Styling Agent

The word "styling agent" in the context of this specification is used in a broad sense which covers all hair cosmetic materials used for hair styling, where any types of aerosol spray, pump-type hair spray, foam-type hair spray,

hair mist, styling lotion, hair cream and hair oil are included. The styling agent is generally prepared by dissolving and/or dispersing a polymer having a styling performance in a solvent such as water and/or alcohols such as ethanol and isopropanol. In the present invention, the above-described block copolymer can be used as the polymer having a styling performance in a singular manner, or in combination with publicly-known general styling polymers of cationic, anionic, nonionic or amphoteric type.

[0064]

Publicly-known cationic polymers applicable to hair styling include ether formed by hydroxycellulose and glycidyl trimethylammonium chloride (Leoguard G, trade name, product of Lion Corporation)), Polymer JR-30M-125 and -400 (trade names, products of Union Carbide)), quaternized product of vinylpyrrolidone-dimethylaminoethyl methacrylate copolymer (Gafquat 734 and 755 , trade names, products of GAF)), dimethyldiallylammonium chloride polymer (Merquat 100, trade name, product of Merck), and dimethyldiallylammonium chloride acrylamide copolymer (Merquat 550, trade name, product of Merck). Anionic polymers for the same purpose include copolymer of (meth)acrylate and alkyl methacrylate (Diahold, trade name, product of Mitsubishi Chemical Corporation), Plascize (trade name, product of Goo Chemical Co., Ltd.); and copolymer of monoalkyl maleate and methyl vinyl ether (trade name, Gantrez (product of ISP)). The nonionic polymers can be exemplified by polyvinylpyrrolidone polymer (PVP, trade name, product of ISP), and copolymer of vinylpyrrolidone and

vinyl acetate (Luviskol, trade name, product of BASF AG)). The amphoteric polymers can be exemplified by methacrylic ester copolymer (Yukaformer AM-75W, trade name, product of Mitsubishi Chemical Corporation).

[0065]

In an embodiment of hair cosmetic material (mousse) which can be injected in a foam state, the composition thereof is preferably adjusted so that the block copolymer accounts for 0.01 to 10% by weight, publicly-known styling polymer for 0 to 15% by weight, nonionic surfactant for 0.1 to 5% by weight, liquefied gas for 3 to 25% by weight, and water-soluble solvent mainly composed of water for 60% by weight to the residual portion. It is preferable herein that the hair cosmetic material is prepared so as to contain water in a content of 60% by weight or above. For an embodiment of gel, the composition thereof is preferably adjusted so that the block copolymer accounts for 0.01 to 10% by weight, publicly-known styling polymer for 0 to 15% by weight, gel base for 0.1 to 3% by weight, and water for 72% by weight to the residual portion. For an embodiment of hair spray, the composition thereof is preferably adjusted so that the block copolymer accounts for 0.01 to 10% by weight, publicly-known styling polymer for 0 to 15% by weight, solvent for 30 to 80% by weight, and injection agent for 10 to 70% by weight.

[0066]

The nonionic surfactant applicable to hair mousse include sorbitan fatty acid ester, glycerin fatty acid ester, polyoxyethylenesorbitan fatty acid ester,

polyethylene glycol fatty acid ester, polyoxyethylenealkyl ether, polyoxyethylenealkyl phenyl ether, polyoxyethylene castor oil, hardened polyoxyethylene castor oil and fatty acid alkanolamide. The injection aid applicable to spray or mousse include liquefied gases such as liquefied petroleum gas, dimethyl ether and halogenated hydrocarbon; and compressed gas such as air, carbon dioxide gas and nitrogen gas.

[0067]

(2) Conditioning Function Providing Agent

The word "conditioning function providing agent" in the context of this specification is used in a broad sense which covers all hair cosmetic materials used for hair conditioning, where any product forms of shampoo, rinse and permanent wave liquid are included. The hair cosmetic materials include those using, as a solvent, water and/or alcohols such as ethanol and isopropanol, which are exemplified by shampoo, rinse and permanent wave liquid; and those using, as a solvent, alcohols such as ethanol and isopropanol, or alcohols and/or hydrocarbons having a boiling point from 50°C to 300°C, which are exemplified by hair treatment. Similarly to the case of the above-described styling agent, the block copolymer may be used as a polymer having a conditioning performance in an singular manner, or in combination with generally-used conditioning polymers of cationic, anionic, nonionic or amphoteric type.

[0068]

In an embodiment of shampoo, it is prepared by adding the block copolymer to any publicly-known anionic,

amphoteric or nonionic surfactant base. The anionic surfactant base can be exemplified by N-(fatty acid)acyl-N-methyl- β -alanine salt such as N-coconyl-N-methyl- β -alanine sodium salt and N-myristoyl-N-methyl- β -alanine sodium salt; the amphoteric surfactant base is exemplified by cocoacidpropyl betaine, dimethyllauryl betaine, bis(2-hydroxyethyl)lauryl betaine, cyclohexyllaurylamine oxide, dimethyllaurylamine oxide and bis(2-hydroxyethyl)laurylamine oxide; and the nonionic surfactant base is exemplified by stearic acid diethanol amide, palm oil fatty acid diethanol amide, sorbitan sesquioleate and polyoxyethylene stearyl ether.

[0069]

In an embodiment of rinse, it is prepared by adding the block copolymer to any publicly-known cationic surfactant base. The cationic surfactant base is exemplified by stearyl trimethyl ammonium chloride, distearyl dimethyl ammonium chloride and stearyl dimethyl benzyl ammonium chloride. In an embodiment of permanent wave liquid, it is prepared by adding the block copolymer to any publicly-known oxidizing agents such as bromate salts and perboric acid, and reducing agents such as thioglycolic acid and its salt, and cysteine.

[0070]

In an embodiment of hair treatment, it is prepared by adding the block copolymer in combination with, or in place of any publicly-known cationic surfactant base, and/or cationic polymers such as cationic polypeptide, cationic cellulose and cationic polysiloxane. As the cationic

surfactant base for hair treatment, those listed typically for the rinse are also available.

[0071]

The hair cosmetic materials in either embodiment of styling agent and conditioning function providing agent can be added with, if necessary, other arbitrary component, besides the foregoing various components within a range not affective to the effects of the present invention. Examples of the arbitrary component include hydrocarbons such as liquid paraffin, vaseline, solid paraffin, squalane and olefin oligomer; straight-chain alcohols such as ethanol, lauryl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol, myristyl alcohol, oleyl alcohol and cetostearyl alcohol; branched alcohols such as monostearyl glycerin ether, 2-decyltetradecanol, lanolin alcohol, cholesterol, phytosterol, hexyl dodecanol, isostearyl alcohol and octyl dodecanol; higher fatty acids and their derivatives such as lauric acid, myristic acid, palmitic acid, stearic acid, behenic (behenyl) acid, oleic acid, 1,2-hydroxystearic acid, undecylenic acid, tall oil fatty acid, lanolin fatty acid, isostearic acid, linolic acid, linoleinic acid, γ -linolenic acid and eicosapentaenoic acid;

[0072]

water-soluble natural polymer including plant-origin polymers such as carrageenan, pectin, agar, quince seed (*Cydonia oblonga*), algae colloid (brown algae extract), starch (rice, corn, potato, wheat) and glycyrrhizinic acid; microbe-origin polymers such as xanthan gum, dextran, pullulan; and animal-origin polymers such as collagen and

gelatin; cellulosic polymers such as methylcellulose, ethylcellulose, methylhydroxypropylcellulose, hydroxyethylcellulose, sodium cellulose sulfate, hydroxypropylcellulose, sodium carboxymethylcellulose (CMC), crystalline cellulose and cellulose powder; semi-synthetic, water-soluble polymers such as sodium arginate and propylene glycol alginate ester;

[0073]

vinyl-base polymers such as polyvinyl alcohol, polyvinyl methyl ether, polyvinyl pyrrolidone, carboxyvinyl polymer (Carbopol); polyoxyethylene-base polymers such as polyethylene glycols 20,000, 4,000,000 and 600,000; synthetic water-soluble polymers such as polyethyleneimine; inorganic water-soluble polymers such as bentonite, AlMg silicate (Veegum), labonite, hectorite and silisic anhydride; silicones such as volatile silicone oil, silicone polymer, silicone rubber and alkyl-modified silicone; N-(fatty acid)acyl-L-glutamate salt such as monosodium N-lauryl-L-glutamate, N-(palm oil fatty acid)-L-glutamate monotriethanolamine, monosodium N-myristic acid acyl-L-glutamate, monosodium N-(mixed fatty acid)acyl-L-glutamate;

[0074]

N-(fatty acid)-N-methyltaurine salt such as lauric acid methyltaurine sodium salt and palm oil fatty acid methyltaurine sodium salt; salts of N-(fatty acid) sarcosine condensate such as sodium lauroylsarcosinate and sodium cocoyl sarcosinate; surfactants such as sodium acylsarcosinate, sodium acylglutamate, sodium acyl- β -alanine, acyl taurate, lauryl sulfate, lauryl

dimethylaminoacetate betaine, alkyl trimethyl ammonium chloride and polyoxyethylene-hardened castor oil;

[0075]

sequestering agent such as 1-hydroxyethane-1,1-diphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid tetrasodium salt, EDTA disodium salt, EDTA trisodium salt, EDTA tetrasodium salt, sodium citrate, sodium polyphosphate, sodium metaphosphate and gluconic acid; various UV absorbing agent such as 3-(4'-methylbenzylidene)-d,1-camphor, 3-benzylidene-d,1-camphor, urocanic acid, urocanic acid ethyl ester, 2-phenyl-5-methylbenzoxazole, 2,2'-hydroxy-5-methylphenylbenzotriazole, 2-(2'-hydroxy-5'-*t*-octylphenyl)benzotriazole, 2-(2'-hydroxy-5'-methylphenylbenzotriazole, dibenzalazine, dianisoylmethane, 4-methoxy-4'-*t*-butyldibenzoylmethane, 5-(3,3-dimethyl-2-norbornylidene)-3-pentane-2-one, and those of benzoic acid-base, anthranilic acid-base, salicylic acid-base, cinnamic acid-base and benzophenone-base;

[0076]

emulsifying agent such as glyceryl monostearate, seryl monostearate, sorbitan monopalmitate, polyoxyethylene cetyl ether and polyoxyethylene sorbitan monolaurate; moisturizers such as (poly)ethylene glycol, (poly)propylene glycol, glycerin, 1,3-butylene glycol, maltitol, sorbitol, chondroitin sulfate, hyaluronic acid, atelocollagen, cholesteryl-1,2-hydroxystearate, sodium lactate, bile acid salt, dl-pyrrolidone carboxylate salt and short-chain soluble collagen; antibacterial agent such as hinokitinol, hexachlorophene, benzalkonium chloride, trichlorocarbanilide

and pituitol; vasodilators such as carpronium chloride; refreshing agent such as menthols; stimulator such as benzyl nicotinate; vitamins such as vitamin A, B, C, D and E; disinfectant/antiseptic agent such as chlorhexidine gluconate, isopropyl methyl phenol and *p*-oxybenzoate ester; [0077]

chelating agent such as protein hydrolysate, amino acid, plant extract and EDTA-Na; pH adjuster such as succinic acid, sodium succinate and triethanolamine; foam increasing agent; foaming agent; foam stabilizer; injection agents for use in aerosol product, such as liquefied petroleum gas and dimethyl ether; sequestering agent; mildewproof agent; emulsifier; conditioner; thickener; antioxidant; solubilizing agent; rosin; hydrotrope; hair tonic; crude drugs; dye; and flavoring ingredient.

[0078]

(Skin and Nail Cosmetic Materials)

Forms of the skin and nail cosmetic materials are not specifically limited, where the skin cosmetic materials include basic cosmetic materials such as cream and milky lotion, and make-up materials such as foundation, face powder, cheek color, eyeshadow and lip color. Nail cosmetic materials include nail color, nail care cream, nail enamel, base coat for nail enamel, and top coat for nail enamel.

[0079]

In embodiments of the skin care and nail care cosmetic materials, the block copolymer is preferably contained in the cosmetic material in an amount of 1 to 30% by weight. The skin care and nail care cosmetic materials can be

manufactured by dissolving, emulsifying or dispersing a block-copolymer-containing component to be blended into any of water, alcoholic solvents such as ethanol, ester-base solvent such as ethyl acetate, ketone-base solvent such as methyl ethyl ketone, and hydrocarbons such as liquid paraffin and vaseline.

[0080]

[Examples]

The following paragraphs will specifically describe the present invention referring to exemplary manufacture and embodiments, where it is to be understood that the present invention is by no means limited to these exemplary manufacture and embodiments.

[Example 1] (Exemplary Manufacture of 2-Ethylhexyl Acrylate/*t*-Butyl Acrylate-Base Block Copolymer)

In a nitrogen-replaced reaction vessel equipped with a thermocouple and a stirring propeller, 165 mg of copper (I) bromide was placed and then heated to 80°C. The content of the reaction vessel, under the nitrogen atmosphere and stirring at 250 rpm, was further added with a mixed solution containing 692 mg of dimethyl-2,6-dibromoheptane dioate, 184 g of 2-ethylhexyl acrylate, 398 mg of pentamethyldiethylene triamine and 88 g of dimethylformamide. After stirred for 3 hours, the reaction vessel was quickly cooled in an ice bath to thereby terminate the reaction. The reaction solution was added with a mixed solution of tetrahydrofuran and water to separate into a layer containing polymer and a layer containing catalyst, and, after the copper bromide was removed, the layer containing polymer was added dropwise to

a large amount of methanol to allow the polymer to re-precipitate, and the solvent was removed by filtration. It was found that the inversion rate of 2-ethylhexyl acrylate was 50 %. The resultant polymer (occasionally referred to as "poly 2-ethylhexylacrylate macro-initiator", hereinafter) was found to have a weight-average molecular weight (M_w) of 33,000, number-average molecular weight (M_n) of 24,000, and molecular weight distribution (M_w/M_n) of 1.38.

[0081]

In a nitrogen-replaced reaction vessel equipped with a thermocouple and a stirring propeller, 28.6 mg of copper (I) bromide and 9.33 mg of copper (II) bromide was placed and then heated to 80°C. The content of the reaction vessel, under the nitrogen atmosphere and stirring at 250 rpm, was further added with a mixed solution containing 48 g of poly 2-ethylhexyl acrylate macro-initiator, 128 g of *t*-butyl acrylate, 79.7 mg of pentamethyl diethylene triamine, and 53 g of dimethylformamide. After stirred for 2 hours, the reaction vessel was quickly cooled in an ice bath to thereby terminate the reaction. The reaction solution was added with a mixed solution of tetrahydrofuran and water to separate into a layer containing polymer and a layer containing catalyst, and the layer containing polymer was allowed to pass through an aluminum silicate column (Kyoward 700SN, product of Kyowa Chemical Industry Co., Ltd.) to thereby completely remove copper bromides, the eluate was dropped into a large amount of methanol to thereby allow the polymer to re-precipitate, and the solvent was removed by filtration. The resultant polymer was found

to have a weight-average molecular weight (M_w) of 56,000, number-average molecular weight (M_n) of 39,800, and molecular weight distribution (M_w/M_n) of 1.41.

Weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer calculated from M_n were found to be 60% by weight and 40% by weight, respectively. The weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer were also confirmed by $^1\text{H-NMR}$. The obtained block copolymer was a triblock copolymer having a formulation of poly(*t*-BA)/poly(2EHA)/poly(*t*-BA).

[0082]

Twenty one grams of thus obtained triblock copolymer of 2-ethylhexyl acrylate and *t*-butyl acrylate was dissolved into 480 ml of 1,4-dioxane. The mixture was then added with 33 mL of 6 mol/L hydrochloric acid, and refluxed under heating in an oil bath at 120°C for 6 hours. The mixture was then cooled, the solvent was condensed under reduced pressure, the residue was re-precipitated in a large amount of hexane, and the solvent was removed by filtration. The obtained polymer was washed with a large amount of water, and dried under reduced pressure to thereby obtain block copolymer P-1.

Ratio of hydrolysis of thus obtained block copolymer P-1 was confirmed by acid value titration using a 0.1 mol/L aqueous potassium hydroxide solution, and was found to be 61%. Glass transition temperature (T_g) was found to be -50°C for the 2-ethylhexyl acrylate block, 43°C for the *t*-butyl acrylate block and 107°C for the acrylic acid block. These glass transition temperatures were found to be nearly

equal to those of the homopolymers of the monomers respectively.

[0083]

[Exemplary Manufacture 2] (Exemplary Manufacture of 2-Ethylhexyl Acrylate/*t*-Butyl Acrylate-Base Block Copolymer P-2)

A poly 2-ethylhexyl acrylate macro-initiator was produced in the same manner as Example 1, except that the stirring was proceeded for 2 hour using 173 mg of copper (I) bromide, 697 mg of dimethyl-2,6-dibromoheptane dioate, 184 g of 2-ethylhexyl acrylate and 419 mg of pentamethyl diethylene triamine. It was found that the inversion rate of 2-ethylhexyl acrylate was 50 %. The obtained polymer was found to have a weight-average molecular weight (Mw) of 23,300, number-average molecular weight (Mn) of 16,400, and a molecular weight distribution (Mw/Mn) of 1.41.

[0084]

In a nitrogen-replaced reaction vessel equipped with a thermocouple and a stirring propeller, 717 mg of copper (I) bromide and 58.3 mg of copper (II) bromide was placed and then heated to 80°C. The content of the reaction vessel, under the nitrogen atmosphere and stirring at 250 rpm, was further added with a mixed solution containing 30 g of poly 2-ethylhexyl acrylate macro-initiator, 151 g of *t*-butyl acrylate, 1g of pentamethyl diethylene triamine, and 66 g of dimethylformamide. After stirred for 3 hours, the reaction vessel was quickly cooled in an ice bath to thereby terminate the reaction. After that, the reaction solution was treated in the same manner as Example 1, and, thus, a

copolymer was obtained. The resultant polymer was found to have a weight-average molecular weight (M_w) of 45,000, number-average molecular weight (M_n) of 25,400, and molecular weight distribution (M_w/M_n) of 1.77. Weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer calculated from M_n were found to be 47% by weight and 53% by weight, respectively. The weight fractions of 2-ethylhexyl acrylate and *t*-butyl acrylate in the block copolymer were also confirmed by $^1\text{H-NMR}$. The obtained block copolymer was a triblock copolymer.

[0085]

Eighteen grams of thus obtained triblock copolymer of 2-ethylhexyl acrylate and *t*-butyl acrylate was dissolved into 500 ml of 1,4-dioxane. The mixture was then added with 36 mL of 6 mol/L hydrochloric acid, and refluxed under heating in an oil bath at 120°C for 20 hours. The mixture was then cooled, the solvent was condensed under reduced pressure, the residue was re-precipitated in a large amount of hexane, and the solvent was removed by filtration. The obtained polymer was washed with a large amount of water, and dried under reduced pressure to thereby obtain block copolymer P-2.

Ratio of hydrolysis of thus obtained block copolymer P-2 was confirmed by acid value titration using a 0.1 mol/L aqueous potassium hydroxide solution, and was found to be 50%. Glass transition temperature (T_g) was found to be -50°C for the 2-ethylhexyl acrylate block, 43°C for the *t*-butyl acrylate block and 107°C for the acrylic acid block. These glass transition temperatures were found to be nearly

equal to those of the homopolymers of the monomers respectively.

[0086]

On the other hand, seventeen grams of thus obtained triblock copolymer of 2-ethylhexyl acrylate and *t*-butyl acrylate obtained in Example 2 was dissolved into 450 ml of 1,4-dioxane. The mixture was then added with 6 mL of 6 mol/L hydrochloric acid, and refluxed under heating in an oil bath at 120°C for 20 hours. The mixture was then cooled, the solvent was condensed under reduced pressure, the residue was re-precipitated in a large amount of hexane, and the solvent was removed by filtration. The obtained polymer was washed with a large amount of water, and dried under reduced pressure to thereby obtain block copolymer P-3.

Ratio of hydrolysis of thus obtained block copolymer P-3 was confirmed by acid value titration using a 0.1 mol/L aqueous potassium hydroxide solution, and was found to be 26%. Glass transition temperature (T_g) was found to be -50°C for the 2-ethylhexyl acrylate block, 43°C for the *t*-butyl acrylate block and 107°C for the acrylic acid block. These glass transition temperatures were found to be nearly equal to those of the homopolymers of the monomers respectively.

[0087]

The molecular weights and molecular weight distributions were measured by GPC through a polystyrene gel column using tetrahydrofuran as a mobile phase, and determined on polystyrene basis.

The glass transition temperatures were measured by DSC (differential scanning calorimetry) at a temperature elevation speed of 20°C/min conforming to JIS K7121. In the following examples, they were measured in the same manner.

[0088]

[Example 3] (Exemplary Manufacture of Random Copolymer (Pc-1))

A five-necked flask is attached with a reflux condenser, a dropping funnel, a thermometer, a nitrogen-replacement glass tube and a stirrer, 60 parts by weight of 2-ethylhexyl acrylate, 40 parts by weight of acrylic acid and 100 parts by weight of ethanol were placed therein, 1.0 weight part of α, α' -azobis(isovaleronitrile) was added, and the mixture was refluxed at 80°C under nitrogen-replaced atmosphere for 10 hours so as to proceed polymerization. The obtained copolymer was neutralized by 25% using a 20% aqueous KOH solution. Glass transition point of the obtained copolymer was found to be -6 °C. The random copolymer was named as P-4.

[0089]

Compositions, expressed in ratio by weight, of the individual copolymers obtained in the above were EHA/TBA/AA=60/16/24 for block copolymer P-1, EHA/TBA/AA=47.2/26.3/26.5 for block copolymer P-2, EHA/TBA/AA=47.2/39.3/13.5 for block copolymer P-3, and EHA/AA=60/40 for random copolymer P-4, where EHA is an abbreviation for 2-ethylhexyl acrylate, TBA is for *t*-butyl acrylate, and AA for acrylic acid.

And a commercially-available, anionic random copolymer

(maleic monoalkyl ester/methyl vinyl ether copolymer, Gantrez A-425 (trade name, product of ISP)) was additionally used as P-5.

[0090]

Properties (Young's modulus and elongation percentage) films formed of P-1 to 5 were measured.

As a sample, a strip of film formed of each polymer, having a thickness of 90 ± 15 μm , a width of 10 mm and a length of 20 mm, was used. The film was used after being dried for one week naturally. With respect to the samples, the tensile test was carried out under a tensile speed of 20 mm/min conforming to JIS K7161, to thereby measure Young's modulus and fracture-point elongation percentage. Results of the measurement were shown in Table 1.

[0091]

Block copolymers P-1 to 5 were neutralized using a 20% aqueous potassium hydroxide solution, and respectively added with a mixed solution of water and ethanol so as to adjust the concentration thereof to 3% by weight, to thereby prepare pump-type hair spray compositions. Each of thus obtained hair spray composition was applied to the hair, and evaluated for its styling ability, style-keeping performance, tackiness, flaking property, feeling of touch and washability according to the evaluation criteria shown below. Results were shown in Table 1.

[Style-Keeping Ability (Styling Performance)]

A hair yarn bundle of 23 cm in length and 2.0 g in weight was dipped in a 3% polymer solution, taken out, lightly squeezed, wound around a 1-cm diameter rod, and

allowed to dry. The hair yarn bundle was removed from the rod, and a curled sample was obtained (L_0 in length). The hair bundle was vertically hung for 3 hours in a thermo-hygrostat chamber preliminarily conditioned at 20°C, 90% RH over 3 hours, and then measured for its length (L_2), curl-retention ratio (%) was calculated from the equation below, and evaluated according to the following criteria.

$$\text{Curl-retention ratio (\%)} = [(23 - L_2) / (23 - L_0)] \times 100$$

◎ : Curl-retention ratio of 85% to 100%

○ : Curl-retention ratio of 60% or more and less than 85%

△ : Curl-retention ratio of 30% or more and less than 60%

× : Curl-retention ratio of 0% or more and less than 30%

[0092]

[Washability]

The hair yarn bundle was processed similarly to as described in the style-keeping performance test described in the above, the resultant curled hair yarn bundle was allowed to stand under a thermo-hygrostatic condition of 23°C, 60% RH, dipped in a 10% aqueous solution of an anionic surfactant (sodium polyoxyethylene laurylsulfate) at 40°C for one hour, rinsed with warm water at 40°C, dried, and whether the polymer remains on the hair yarn bundle or not was checked by visual observation and finger touch, and evaluated according to the following criteria.

○ : No residual polymer confirmed visually and tactually.

△ : A slight amount of residual polymer visually confirmed.

× : Residual polymer visually confirmed.

[0093]

[Evaluation of Tacky Touch of Hair]

A hair yarn bundle of 15 cm in length and 10 g in weight was coated with approximately 2 g of each sample, and allowed to stand at room temperature. Thirty minutes after, the tacky touch was evaluated through sensory test by a ten-membered panel, according to the following criteria.

- ◎ : None of 10 panelists recognized tacky touch.
- : One or two panelists recognized tacky touch.
- △ : Three to five panelists recognized tacky touch.
- × : Seven or more panelists recognized tacky touch.

[0094]

[Evaluation of Finger Touch of Hair]

A hair yarn bundle of 15 cm in length and 10 g in weight was coated with approximately 2 g of each sample, and allowed to stand at room temperature. Thirty minutes after, the feel to the touch was evaluated through sensory test by a ten-membered panel, according to the following criteria.

- ◎ : All of ten panelists recognized that it was good to the touch.
- : Eight or more of ten panelists recognized that it was good to the touch.
- △ : Four to seven of ten panelists recognized that it was good to the touch.
- × : Only one to three of ten panelists recognized that it was good to the touch.

[0095]

[Styling Ability Test (Bending Strength of Hair Yarn Bundle)]

A hair yarn bundle of 15 cm in length was coated with

0.7 g of each sample, immediately shaped in 2-cm width, dried, and allowed to stand for one hour in a thermo-hygrostat chamber conditioned at 23°C, 60% RH. The sample was then placed on the supports 65 mm distant from each other and bent at the center thereof under a constant speed, and maximum load was measured and evaluated according to the following criteria.

- : The maximum load was 200 g or above, and the coated hairs were soft to the touch and there was no incompatibility after measurement.
- △ : The maximum load was 100 g or more, and the coated hairs were soft to the touch, but there was a certain level of incompatibility after measurement.
- × : The maximum load was less than 100 g, and the coated hairs were not soft to the touch, and there was incompatibility after measurement.

[0096]

[Style-Keeping Ability Test (Hair Yarn Bundle Bending Test)]

After the style-keeping performance test, maximum load after the hair yarn bundle was broken was evaluated according to the following criteria.

- : Maximum load was 15 g or more.
- △ : Maximum load was 10 g or more and less than 15 g.
- × : Maximum load was less than 10 g.

[0097]

[Flaking]

A constant volume of each sample was sprayed to the hair yarn bundle, completely dried, combed, and the amount of dropped polymer flakes (state of flaking) remaining on

the hair yarns was observed under a stereo-microscope (× 20). Evaluation criteria are as shown below.

○ : Peeled polymer not observed, no flaking.

△ : A slight amount of peeled polymer observed, slight flaking

× : A lot of peeled polymer observed, considerable flaking.

[0098]

[Table 1]

	Examples			Comparative Examples	
Polymer	P-1	P-2	P-3	P-4	P-5
Curl-retention ratio	◎	◎	○	○	×
Young's modulus Mpa	50	120	200	10	150
fracture-point elongation percentage %	>500	280	20	>500	3
Washability	○	○	○	×	△
Styling Ability	○	○	○	△	○
Style-Keeping Performance	○	○	○	×	×
Finger Touch of Hair	◎	◎	○	△	△
Tackiness	○	◎	◎	△	△
Flaking	○	○	○	△	△

[0099]

It was found from the results shown in Table 1 that the block copolymers P-1 to 3 were superior to random copolymer P-4 and conventional anionic polymer P-5 in all performances of hair washability, styling ability, moisture resistance and smooth touch. It was also found that the properties of the films formed of the block copolymers P-1 to 4 respectively were varied depending on the formulations of the block copolymers, and that, in particular, the properties of the films were changed drastically on a ratio of a hard segment (t-butyl acrylate) and a soft segment (2-ethylhexyl acrylate) reaching 50%. And it was suggested that the elongation ratio and the curl-retention degree were varied depending on a content of acrylic acid.

[0100]

In the following description, amounts of polymer used for the actual formulations in "% by weight" are expressed on the solid basis.

[Example 4]

A shampoo composition shown below was prepared.

	(% by weight)
Sodium polyoxyethylene lauryl sulfate (3EO adduct)	16%
Lauroyl diethanol amide	2%
"P-1"	1.5%
Flavoring ingredient	0.2%
Mildewproofing agent	0.1%
Colorant	trace amount
Pure water	for balancing
Total	100%

[0101]

Use of the composition as a shampoo resulted in smooth combing of the washed hair, excellent luster or gloss of the dried hair, and was successful in giving smooth but volume-raised touch. Repetitive shampooing did not result in adverse effects such as producing tacky touch. The similar results were obtained from the compositions using block copolymers P-2 and P-3 respectively.

[0102]

[Example 5]

A rinse composition below was prepared.

	(% by weight)
Steraryl trimethyl ammonium chloride	1.5%
Cetanol	2%
"P-2"	1.5%
Flavoring ingredient	0.2%
Pure water	for balancing
Total	100%

[0103]

Use of the composition as a rinse resulted in easy and smooth combing of the rinsed hair, and excellent luster or gloss of the dried hair. Repetitive rinsing did not result in adverse effects such as producing tacky touch. The similar results were obtained from the compositions using block copolymers P-1 and P-3 respectively.

[0104]

[Example 6]

The mother liquor for dilution shown below was put in a spray can and the can was filled with a liquefied

petroleum gas, to thereby prepare a hair spray composition.

Mother liquor for dilution	(% by weight)
"P-2"	1%
Absolute ethanol	49%
Total	50%
Liquefied petroleum gas (3 kg/cm ² G, 20°C)	50%

[0105]

Use of the composition as being sprayed to the hair resulted in an excellent style-keeping performance even with a small content of the polymer, and gave desirable gloss, luster and smooth touch of the hair. The similar results were obtained from the compositions using block copolymers P-1 and P-3 respectively.

[0106]

[Example 7]

A hair spray was prepared using random copolymers P-4 and P-5. Use of a composition having a formulation same as that of Example 6 as being sprayed to the hair resulted in only a poor style-keeping performance due to a small content of the polymer, and failed in giving desirable gloss, luster and smooth touch.

[0107]

[Example 8]

A foam-type aerosol composition was prepared similarly to as described in Example 6.

Mother liquor for dilution	(% by weight)
"P-2"	2%
Polyoxyethylene cetyl ether (10 EO adduct)	0.3%

Polyoxyethylene cetyl ether (2 EO adduct)	0.1%
Pure water	85.6%
Total	88%
Liquefied petroleum gas (3 kg/cm ² G, 20°C)	12%

[0108]

The composition applied to the hair gave excellent results similarly to as described in Example 6 in the above. The similar results were obtained from the compositions using block copolymers P-1 and P- 3 respectively.

[0109]

[Example 9]

A styling lotion composition shown below was prepared.

	(% by weight)
"P-2"	3%
Pure water	60%
Absolute ethanol	37%
Total	100%

[0110]

The composition applied to the hair gave excellent results similarly to as described in Example 9 in the above. The similar results were obtained from the compositions using block copolymers P-1 and P-3 respectively.

[0111]

[Example 10]

A compositions were prepared similarly to as described in Example 9 using comparative random copolymers P-4 and P-5 respectively, but use of the composition as a styling lotion resulted in only a poor style-keeping performance, and failed in giving desirable gloss, luster and smooth touch.

[0112]

[Example 11]

A gel composition shown below was prepared.

	(% by weight)
"P-3"	1%
Carbopol 940*	0.5%
(adjusted to pH7.5 with aqueous KOH solution)	
Pure water	98.5%
Total	100%

*product of B.F.Goodrich Chemical Co.

[0113]

The composition applied as a gel to the hair resulted in an excellent hair-style-keeping performance, and in desirable luster, gloss and smooth touch. Repetitive coating of the gel composition and hair wash did not cause tacky touch, or any adverse effects of incompatible sense due to accumulation. The similar results were obtained from the compositions using block copolymers P-1 and P-2 respectively.

[0114]

[Example 12 (Skin Care Cosmetic Material)]

Skin care cosmetic material 1 was prepared according to the formulation shown in Table 2 below.

[0115]

Thus obtained skin care cosmetic material 1 was applied to the skin. It was found that the film obtained after drying gave smooth and desirable touch, rather than incompatible sense nor tacky touch.

[0116]

Skin care cosmetic material 2 was prepared similarly to as described in the above except that a 6% ethanol solution of a cationic polymer (trade name: JR-400, product of Union Carbide) was used, in place of block copolymer P-1, according to the formulation shown in Table 2. Application of the skin care cosmetic material 2 on the skin resulted in tacky touch, rather than smooth touch.

Skin care cosmetic material 3 was prepared similarly to as described in the above except that a 6% ethanol solution of an anionic polymer (trade name: Gantretz A425, product of ISP) was used, in place of block copolymer P-1, according to the formulation shown in Table 2. Application of the skin care cosmetic material 3 on the skin resulted in tacky touch, rather than smooth touch, and the resultant film was peeled off only by a several times of rubbing.

[0117]

[Table 2]

		Skin Cosmetic 1	Skin Cosmetic 2	Skin Cosmetic 3
Polymer	Polymer P-1 (6 % solution)	50%	—	—
	Cationic polymer (6 % solution) "JR-400"	—	50%	—
	Anionic polymer (6 % solution) "A425"	—	—	50%
Poly ether-modified silicone "SH3771C" (manufactured by TORAY DOW CORNING CO LTD)		0.3%	0.3%	0.3%
Water		49.7%	49.7%	49.7%

[0118]

[Example 13(Nail Care Cosmetic Material)]

The components listed below were dispersed and mixed in a bead mill for one hour, to thereby prepare nail care cosmetic material 1.

	(% by weight)
"P-3"	40.0%
	(10.0% on solid basis)
Isopropanol	10.0%
Red No. 226	0.1%
Titanium oxide	4.9%
Ethanol	40.0%
	(65.0% as total ethanol)
Bentonite	5.0%
(trade name: Bentone EW, product of National Lead Company)	

[0119]

The composition applied on the nail dried quickly, and the resultant film was less peelable and showed a good film-keeping property. The similar results were obtained from the compositions using block copolymers P-1 and P-2 respectively.

[0120]

[Effect of the invention]

As described above, according to the present invention, it is possible to provide a cosmetic polymer composition and a cosmetic material capable of satisfying a plurality of performances required for the cosmetic material at the same time by using a polymer having two or more properties.

[Name of document] Abstract

[Abstract]

[Object] To provide a cosmetic polymer composition and a cosmetic material capable of satisfying a plurality of performances required for the cosmetic material at the same time by using a polymer having two or more properties.

[Means for solving the problems] A cosmetic polymer composition comprising a block copolymer having a unit derived from a compound having an ethylenic unsaturated bond, having a number-average molecular weight of 1.0×10^3 to 1.0×10^6 , and having two or more glass transition points or melting points; and a cosmetic employing the composition are provided. Preferably, the cosmetic polymer composition wherein the block copolymer comprises at least one block composed of a unit having a hydrophilic group; and a cosmetic employing the composition; were provided.

[Representative drawing] None